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In-situ NMR Study of Hydrothermal Reactions of Hazardous Chlorinated Organic Compounds: CH_2Cl_2

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Hydrothermal decomposition of a hazardous chlorinated organic compound, dichloromethane, has been investigated using *in-situ* NMR spectroscopy. It is found that the hydrolysis of dichloromethane yields methanediol as an intermediate. Methanediol is a hydrated form of formaldehyde and easily transformed into methanol and formic acid under basic conditions. In the temperature range of 70-140 °C, the Cannizzaro-type reaction occurs: methanediol produces the reduced form, methanol and the oxydized form, formic acid. At higher temperatures between 200 and 250 °C, on the other hand, two methanediol molecules form glycolic acid which has a new C-C bond. The reaction rate constants and activation energies for the dechlorination and the Cannizzaro-type reactions have been obtained.

Keywords : Hydrothermal reaction / *in-situ* NMR spectroscopy / dichloromethane / dechlorination / Cannizzaro reaction

Recently we are alerted that many useful chlorinated organic compounds are biologically and environmentally hazardous. It is thus a main goal of environmental chemistry to establish a reaction scheme which provides nontoxic and recyclable organic compounds from chlorinated organic compounds by reducing the C-Cl bonds as shown in Fig. 1. To achieve this goal, high-temperature and high-pressure water is a desirable medium since it is clean and safe and able to dissolve organic compounds. In order to convert hazardous chlorinated compounds to recyclable compounds, the reduction process in supercritical water (SCWR) is more preferable than the oxidation process (SCWO), as shown in Fig. 1. By the SCWO method, organic compounds are oxidized completely and any useful compounds are not recovered. In contrast, the hydrothermal dechlorination enables one to recycle hazardous chlorinated compounds under milder

conditions. In order to develop an optimal process for recycling hazardous chlorinated compounds, it is essential to understand the dechlorination mechanism. The purpose of this report is to show the power of *in-situ* NMR spectroscopy for gaining insights into the reaction mechanism. By this method, the formation and breakage of chemical bonds can be observed in real time and it is possible to simultaneously characterize not only products but also reaction intermediates. Here we focus on the *in-situ* NMR observation of the hydrothermal reactions of CH_2Cl_2 .

CH_2Cl_2 supplied by Nacalai was used after the stabilizer and impurity were removed. NaOH of guaranteed reagent grade obtained from Nacalai was used without further purification. Water was purified using a Milli-Q Labo. filter system (Milli-Q Pore). Aqueous NaOH solution was prepared by weight; the concentration

INTERFACE SCIENCE — Solutions and Interfaces —

Scope of research
Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR under extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.



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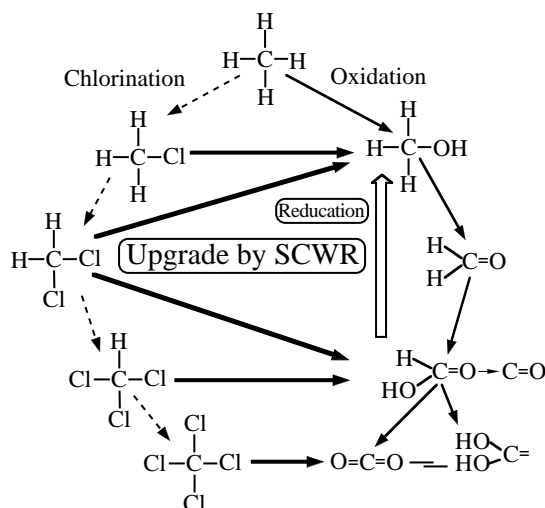
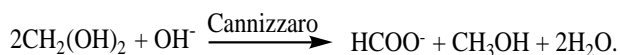


Figure 1. Sub- and supercritical C_1 chemistry of chlorinated organic compounds. For example, CH_2Cl_2 can be converted to useful organic compounds by reduction and oxidation before reaching to the final oxidation states, H_2O and CO_2 .

was 0.5–2.0 M. An amount of CH_2Cl_2 corresponding to 0.8–1.0 M solution was put in a quartz tube, the outer and inner diameters of which were 4.0 and 2.5 mm, respectively, and then water or aqueous NaOH solution was added by using a micro-syringe. The tube was sealed to a length of 7 cm. We used an NMR spectrometer (JNM-EX270, JEOL; 6.35 T) equipped with a high-temperature probe previously applied to the study of supercritical water. We measured 1H and ^{13}C spectra as functions of temperature and NaOH concentration; it took ~10 min to heat the system up to 250 °C. CH_2Cl_2 and CH_3OH were used as reference materials for the 1H and ^{13}C chemical shift measurements. The free induction decay signal was accumulated 8–16 times for 1H and 25000 times for ^{13}C .

The main reaction of methanediol in the temperature range of 70–140 °C is



At higher temperatures (200 and 250 °C), on the other hand, we have found another reaction path of methanediol. From the chemical shifts of 1H and ^{13}C , it is clear that the new product is glycolic acid ($CH_2(OH)COOH$), and the reaction path of the formation of glycolic acid is considered as follows:



According to the time dependence of the concentrations of the intermediate and products at 80 °C, the concentration of methanediol quickly increases and reaches a plateau. The concentrations of methanol and formic acid increase linearly with the time. This indicates that the dechlorination reaction is the rate-determining step and that the Cannizzaro reaction occurs immediately after the dechlorination. In other words, $CH_2(OH)_2$ is further evidenced as an intermediate of the hydrothermal decomposition of CH_2Cl_2 . It is in addition shown at 80 °C that the reaction rate of the Cannizzaro reaction increases with the concentration of OH^- .

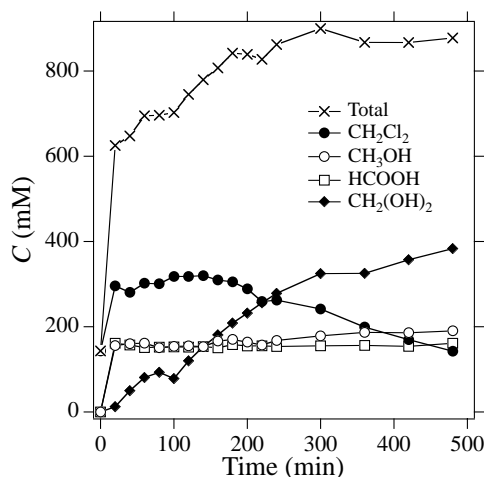
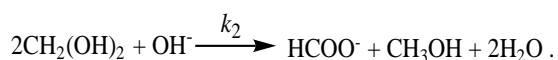
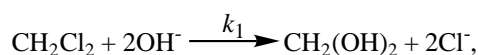


Figure 2. Time dependence of the concentrations of the reactant and products of the hydrothermal reaction of CH_2Cl_2 (0.8 M) in aqueous NaOH solution (1.6 M) at 140 °C.

It is depicted in Fig. 2 how the concentrations of the reactant and products vary with time at 140 °C: at 120 and 130 °C, the time dependences are very similar to that at 140 °C. As expected, the dechlorination at 140 °C is much faster than that at 80 °C. The plateau values for the concentrations of the products indicate that the Cannizzaro reaction is quickly finished. The stationary concentrations of methanol and formic acid produced are almost the same (~170 mM) at 120, 130, and 140 °C. Methanediol increases monotonously with time. When more than 300 min has passed, the concentration of methanol is larger than that of formic acid. This is caused by the cross Cannizzaro-type reaction between methanediol and formic acid, which produces methanol and carbon dioxide as clarified in the previous work on the hydrothermal decomposition of *s*-trioxane.

We also determined the rate constants as functions of the $[OH^-]$ concentration at 80 °C according to the following reaction scheme:



In the low concentration range, the rate constant for the Cannizzaro reaction is almost independent of $[OH^-]$: $k_2 = 5.6 \times 10^{-3}$ and $6.2 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ at 0.5 and 1.0 M, respectively. In 2.0 M solution, on the other hand, k_2 is $15 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ and ~3 times larger than those in 0.5 and 1.0 M solutions. It has been reported that the rate constant is proportional not to $[OH^-]$ but to $[OH^-]^2$ at high concentrations due to the existence of the second ionized state, $CH_2(O^-)_2$, of methanediol: the ability to make the hydride ion H^- is much higher for $CH_2(O^-)_2$ than for $CH_2(OH)O^-$.

It is therefore concluded that the hydrothermal dechlorination of dichloromethane can be achieved efficiently at 250 °C in the presence of a base (NaOH). Such a high temperature is required to compensate for the solubility drop due to the base and to accelerate the rate of the transformation to useful compounds.